

# PATENT SPECIFICATION

NO DRAWINGS

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The inventor of this invention in the sense of being the deviser thereof within the meaning of Section 16 of the Patents Act 1949, is:—IRVIN BRUCE VAN HORN, Post Office Box 172, New Martinsville, United States of America, EUGENE LEROY POWERS, 535 Greenbriar Court, New Martinsville, West Virginia, United States of America, both citizens of the United States of America.

## COMPLETE SPECIFICATION

### Recovery of Amines

We, MOBAY CHEMICAL COMPANY, a corporation organised under the Laws of the State of Delaware, United States of America with its general offices located at Penn Lincoln Parkway West, Pittsburgh 5, Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the recovery of aromatic amines from the distillation residues obtained in the production of aromatic isocyanates.

The digestion with lye of the distillation residue obtained when an aromatic isocyanate is distilled from the solution in which it was prepared has been previously suggested in *Annalen der Chemie*, Volume 562, page 75, 1948. Canadian Patent No. 583,372 also discloses a method of preparing aromatic amines where the distillation residue is heated to 160 to 250°C. with water. This patent also provides for the use of a small amount of alkali, normally an amount of less than one per cent by weight based on the weight of the residue to neutralise the chlorine contained in the distillation residue. Still another patent which mentions the old caustic treatment to recover aromatic diamines is U.S. Patent No. 2,999,873, which contains an incidental disclosure that the residue from the still pot obtained in the production of toluylene diisocyanate by phosgenation of tolylene diamine may be treated with caustic to recover a quantity of the tolylene diamine. While these previously known processes have helped in solving the problem of lost aromatic amine in the production of aromatic isocyanate, the yield of aromatic amine from the residue by treatment with caustic leaves much to be desired.

It is, therefore, an object of this invention to provide an improved process for the recovery of amines from the distillation residue obtained when an aromatic amine is phosgenated to

produce an aromatic isocyanate which is then distilled from the reaction mixture in which it was prepared. Another object of this invention is to provide an improved digestion procedure for these distillation residues. Further objects of this invention include the provision of an improvement in the yield obtained when an aromatic amine is prepared by heating water with the distillation residue obtained in the distillation of aromatic isocyanates as well as the provision of an improved method of recovering 2,4- and 2,6-toluylene diamines from the distillation residues obtained by distilling a toluylene diisocyanate from the solution in which it was prepared by treating the amines with phosgene.

The foregoing objects and others which will become apparent from the following description are accomplished in accordance with the invention which provides for a process for the preparation of aromatic primary mono- and di-amines which comprises heating water and the distillation residue, obtained from the product of phosgenation of an aromatic primary mono- or di-amine after distilling off the corresponding aromatic isocyanate, to a temperature above 250°C. but not above 350°C. As stated above, it has been known previously to react water with the residue obtained when distilling aromatic isocyanates from the reaction mixture in which they are prepared. This invention involves the improvement of carrying out this reaction at a temperature of from 250°C. to 350°C. It is preferable to also use up to 10 per cent by weight of an alkali metal hydroxide in the aqueous solution to obtain an even further improvement in yield.

The process of the invention can be carried out either continuously or batchwise. It is preferred to use the continuous method because this is more readily adaptable to commercial practice and gives improved recovery rates. The process begins by taking the residue from an isocyanate stripping still and placing it in an autoclave. Then sufficient water is added to

react with the residue. It is possible to being either with cold residue which has been allowed to cool from the pot temperature to ambient temperatures and stored for any length of time or, alternatively, the hot residue from the still pot may be slurried with the water and caustic. In either event, if the residue is in too large chunks, it may be necessary to subdivide it merely for the purpose of ease of handling the slurry. The reaction is speeded up by having the residue reduced in size to less than 16 mesh. This may be accomplished with any suitable grinding means. After the slurry of residue, water and, if desired, alkali is formed, it is then passed into a heated zone so that the reaction mixture comes to a temperature of above 250°C. but not above 350°C. The heating can be accomplished in any suitable way directly or indirectly including the injection of high pressure steam directly into the slurry. If steam is used the consequent dilution must be taken into account so that the proper concentration of caustic is maintained if caustic is being used. It is also desirable to have the reactor under pressure of at least 100 psig. but preferably not more than 2500 psig. The reaction mixture is kept at the temperature and, if desired, pressure until the residue has reacted with the water to produce the corresponding aromatic amine. The time varies from a few seconds to several hours depending on the state of subdivision of the residue, the temperature, pressure and the like. Usually a residence time for a continuous process of one to five minutes is sufficient to insure satisfactory yields if the residue is previously reduced to a particle size of 16 mesh or less. The excess water and the aromatic amine formed in the process of the invention are then passed to a recovery zone where carbon dioxide formed in the reaction is flashed off together with some water vapour and a crude product containing water, aromatic amine and by-products is obtained. This crude reaction mixture is then refined by distilling out water and amine. The amine is purified by conventional techniques to prepare a product suitable for many uses including phosgenation to prepare the corresponding isocyanate.

The invention is particularly suitable for the preparation of 2,4- and 2,6-toluylenes essentially free of ortho diamines by reaction of the distillation residue formed when a mixture of about 80 per cent 2,4- and 20 per cent 2,6-toluylene diamine is phosgenated, for example, according to the process of the U.S. Patent No. 2,908,703 and then the toluylene diisocyanates in the ratio of about 80 per cent 2,4- and 20 per cent 2,6-toluylene diisocyanate are distilled from the reaction mixture.

The alkaline solution may be formed with any suitable alkaline material or mixture of materials. The alkali metal bases, including sodium hydroxide and potassium hydroxide are preferred for ease in handling and economics.

The amines prepared are useful for phosgenation to prepare isocyanates which are, in turn, useful as insecticides, coatings, and where polyisocyanates are prepared, for the preparation of polyurethane plastics which may be foams or non-porous elastomers as in U.S. Reissue Patent 24,514 or U.S. Patent 2,729,618. These final products have many well-known commercial uses such as for pillows, in the case of foams and gear wheels in the case of non-porous plastics.

The distillation residue obtained in the production of any aromatic mono- or diisocyanate may be used in the process of this invention such as, for example, the distillation residue obtained in the production of phenyl isocyanate diphenylmethane diisocyanates such as 4,4'-diphenylmethane diisocyanate, naphthalene diisocyanates such as 1,5-naphthalene diisocyanate.

In order that the invention may be more fully understood the following examples, in which parts are by weight unless otherwise specified are given by way of illustration only:

#### EXAMPLE 1

A mixture of 80 per cent 2,4-toluylene diisocyanates and 20 per cent, 2,6-toluylene diisocyanate was prepared by reacting a mixture of 80 per cent 2,4- and 20 per cent, 2,6-toluylene diamine in orthodichlorobenzene with an excess of phosgene according to the procedure described in U.S. Patent No. 2,680,127. The distillation residue obtained in this process was then mixed with water in such proportions that there were 150 parts of residue and 150 parts of water. The reaction was heated in an autoclave to a temperature and pressure sufficient to produce slightly more than 250°C. for one hour. The pressure increased as the reaction proceeded due to evolution of CO<sub>2</sub>. Pressure was regulated by release of CO<sub>2</sub>. The water was removed by distillation followed by distillation of the toluylene diamine. About 44.6 parts of a mixture of 2,4- and 2,6- toluylene diamine was recovered per hundred parts of residue used as a starting material. The foregoing example was repeated at 300°C. and at 330°C. with only minor variations of less than one part per hundred parts of residue in the yield.

#### EXAMPLE 2

The residue of Example 1 was mixed with water in such proportions that there were 150 parts of residue and 150 parts of a mixture of water and sodium hydroxide, said mixture having been prepared by combining 990 parts of water with 10 parts of sodium hydroxide. The reaction mixture was heated in an autoclave to a temperature and pressure sufficient to produce slightly more than 250°C. for 1 hour. The pressure increased as the reaction proceeds due to evolution of CO<sub>2</sub>. Pressure was regulated by release of CO<sub>2</sub>. Water was then removed by distillation followed by distillation of the toluylene diamine. The recovery was 47 parts of a mixture of 2,4- and 2,6-toluylene diamine

per hundred parts of residue. When the foregoing example was repeated at temperatures of 300 and 330°C., an improved recovery of 50 parts of toluylene diamine per hundred parts of residue was obtained.

### EXAMPLE 3

The residue of Example 1 was mixed with an aqueous solution of sodium hydroxide in such proportions that there were 150 parts of residue and 150 parts of aqueous solution prepared by mixing 950 parts of water with 50 parts of sodium hydroxide. The reaction mixture was heated to a temperature of 280°C. for one hour under pressure as in Example 1. The water was removed by distillation followed by distillation of the toluylene diamine. 53.6 parts of a mixture of 2,4- and 2,6-toluylene diamine isomers were obtained per hundred parts of residue.

### WHAT WE CLAIM IS:—

1. A process for the preparation of aromatic primary mono- and di-amines which comprises heating water and the distillation residue, obtained from the product of phosgenation of an aromatic primary mono- or di-amine after distilling off the corresponding aromatic isocyanate, to a temperature above 250°C., but not above 350°C.
2. A process as claimed in claim 1 in which the residue is heated with water which is mixed up to 10 per cent by weight of an alkali metal

hydroxide.

3. A process as claimed in claim 2 in which the alkali metal hydroxide is sodium hydroxide.

4. A process as claimed in any of claims 1 to 3 in which the aromatic primary amine is a mixture of 2,4-toluylene diamine and 2,6-toluylene diamine.

5. A process as claimed in any of claims 1 to 3 in which the aromatic primary amine is aniline.

6. A process as claimed in any of claims 1 to 3 in which the aromatic primary amine is 4,4'-diamino diphenylmethane.

7. A process for the preparation of toluylene diamine which comprises heating water and the distillation residue obtained from the product of phosgenation of toluylene diamine after distilling off corresponding toluylene diisocyanate to a temperature above about 250°C. but not above 350°C.

8. A process for the preparation of aromatic amines substantially as herein described with reference to any one of the Examples.

9. Aromatic amines when prepared by a process as claimed in any of the claims 1 to 8.

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